



# Rhodium catalyzed aqueous biphasic hydroformylation of naturally occurring allylbenzenes in the presence of water-soluble phosphorus ligands

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## ABSTRACT

The rhodium-catalyzed hydroformylation of eugenol was performed in aqueous biphasic systems using various water soluble phosphines: TPPTS (triphenylphosphinetrisulphonated); BDPPETS (bis(diphenylphosphinoethanetetrasulphonated), BDPPPTS (bis(diphenylphosphinopropanetetrasulphonated) and BISBIS (diphosphane 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl disulphonated). The addition of the cationic surfactant CTAB (cetyltrimethylammonium bromide) increased the reaction rate; however, high surfactant concentrations unfavorably affected the reaction selectivity. The regioselectivity of the hydroformylation was strongly depended on the ligand nature. The procedure was successfully extended to other allylbenzenes, i.e., estragole and safrole, producing several fragrance compounds starting from the substrates easily available from natural bio-renewable resources.

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## 1. Introduction

Naturally occurring olefins are a green alternative source of renewable feed stocks for chemical industry. One family of naturally occurring olefins is the allylbenzenes such as eugenol (**1a**), estragole (**1b**) and safrole (**1c**) (Scheme 1) obtained from cloves, sweet basil and parsley, respectively. The hydroformylation of allylbenzenes and isomeric propenylbenzenes gives aldehydes and alcohols of high added-value with interesting properties that are important in the pharmacological, cosmetic, food and fragrance industries [1–4].

Several groups have studied the hydroformylation of allylbenzenes over the years. Kalck et al. [5] reported the hydroformylation of eugenol, estragole, safrole and eugenol-methyl ether using  $[\text{Rh}(\mu\text{-SR})_2(\text{CO})_2\text{L}_2]$  as a catalyst precursor (in which  $\text{L}=\text{PPh}_3$ ,

$\text{P}(\text{OPh})_3$  and  $\text{P}(\text{OMe})_3$ ) and obtained high regioselectivity towards the linear aldehydes (80–96%).

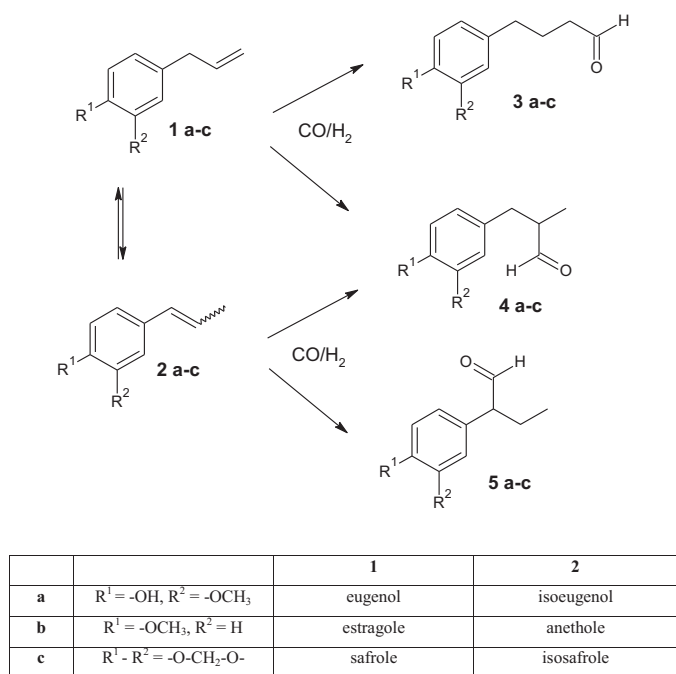
E. dos Santos and coworkers [1] reported the rhodium catalyzed hydroformylation of various allylbenzenes and propenylbenzenes with 97–99% chemoselectivity in the presence of several phosphorous ligands, such as  $\text{P}(\text{OPh})_3$ ,  $\text{PPh}_3$ ,  $\text{P}(\text{Cy})_3$ ,  $\text{P}(\text{CH}_2\text{-Ph})_3$ ,  $\text{P}(\text{n-Bu})_3$ , dppe, dppp, dppb, BISBI, and NAPHOS. The activity and regioselectivity of the Rh-monophosphine systems were found to be strongly depended on the basicity of the ligand. In the Rh-diphosphine systems, the regioselectivity correlated with the bite angle of the ligand used, with wide-angled ligands favouring the formation of linear aldehydes.

Paganelli et al. [2] reported the hydroformylation of *m*-diisopropenylbenzene in homogeneous, heterogeneous and biphasic systems as a first step in the preparation of the monoaldehyde Florhydral, a patented, marine-scented fragrance. The hydroformylation in aqueous-toluene biphasic systems was performed with  $[\text{Rh}(\text{COD})\text{Cl}]_2$  or  $[\text{Rh}(\text{CO})_2(\text{acac})]$  as catalyst precursors and trisulfonated triphenylphosphine (TPPTS) or the biopolymer HSA (human serum albumin) as the ligands.

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**Scheme 1.** Hydroformylation of allylbenzenes and propenylbenzenes.

Some of us have shown a great interest in the biphasic hydrogenation and hydroformylation of olefins and light naphtha cuts with water-soluble rhodium, ruthenium, tungsten and molybdenum precursors [6–10]. Recently, we have shifted our focus towards the functionalization of naturally occurring olefins like allylbenzenes and terpenes, readily available from biomass, in biphasic aqueous media and ionic liquids aiming to obtain high added-value products important in the cosmetic, perfume and pharmaceutical industries [11,12]. Aqueous biphasic hydroformylation represents one of the most promising alternatives to overcome the general problem of homogeneous hydroformylation related with the separation of products and high cost rhodium catalysts. This problem is especially crucial for the separation of high-boiling aldehydes derived from allylbenzenes and terpenes because their distillation in the presence of the catalyst could promote the catalyst decomposition and loss of the metal.

The low water solubility of higher alkenes can result in serious restrictions to perform their aqueous biphasic hydroformylation at reasonable rates. In this case, surfactants [13,14] or cyclodextrins [15,16] can be used as one of the most practical and effective strategies to avoid transfer limitations in aqueous/oil biphasic systems. Cationic surfactants provide the most significant effects in Rh/sulfonated phosphine systems as their positively charged moiety directed to the aqueous phase attract the anionic Rh complex to the water/organic phase interface where the catalyst meets the substrate.

In the present work we report the rhodium-catalyzed hydroformylation of eugenol, estragole and safrole in aqueous biphasic systems giving special attention to the effect of the cationic surfactant cetyltrimethylammonium bromide (CTAB) and the nature of water soluble ligands on these reactions.

## 2. Experimental

### 2.1. General procedures

Eugenol, estragole, and safrole were purchased from Aldrich and bubbled with argon prior to use. Cetyltrimethylammonium bromide (CTAB) was purchased from Aldrich and

used as received. Hydrogen (99.999%) and carbon monoxide (99%) were purchased from Praxair. Bis( $\mu$ -methoxy)(1,5-cyclooctadiene)rhodium(I) ([Rh(COD)( $\mu$ -OMe)<sub>2</sub>] [17], TPPTS (triphenylphosphinetrisulphonated) [18]; BDPPETS (bisdiphenylphosphinoethanetetrasulphonated) [19]; BDPPPTS [20] (bisdiphenylphosphinopropanetetrasulphonated) and BISBIS (diphosphane 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl disulphonated) [21], were prepared according to published procedures. Manipulations under argon were made employing Schlenk techniques. Toluene was refluxed with sodium/benzophenone for 8 h. Deionized water was refluxed under argon for 6 h. After treatment, all solvents were distilled and stored under argon.

### 2.2. Catalytic runs

The catalytic runs were performed in a mechanically stirred stainless steel Parr 4560 bomb coupled with a 4282 control module with a PDI temperature controller, tachometer, and a pressure transducer connected to a field logger apparatus. In a typical experiment the catalyst precursor [Rh(COD)( $\mu$ -OMe)<sub>2</sub>] ( $2.5 \times 10^{-6}$  mol), TPPTS ( $5.0 \times 10^{-5}$  mol) and the phase transfer agent cetyltrimethylammonium bromide (CTAB,  $0.0$ – $2.0 \times 10^{-4}$  mol) were dissolved in 20 mL of deoxygenated water in a Schlenk tube under argon. The solution was transferred into the bomb, and the substrate ( $1.0$ – $2.0 \times 10^{-2}$  mol) was placed in a pressure-equalized reservoir on the top of the bomb. The reactor was pressurized with the desired carbon monoxide pressure (5–20 bar) and then with hydrogen (5–20 bar) up to the desired total pressure. The bomb was heated to the desired temperature (80–120 °C) and kept for one hour under mechanical stirring (750 rpm). The substrate was then added and the register of the syngas pressure drop was initiated. After pressure drop stopped, the reactor was cooled, vented, the organic phase was extracted with toluene (20 mL) and analysed by GC.

### 2.3. Catalyst recycling

The catalytic runs for recycling were performed in a magnetically stirred stainless steel bomb heated in an aluminum block with a PID temperature control. The catalyst precursor [Rh(COD)( $\mu$ -OMe)<sub>2</sub>] ( $2.5 \times 10^{-6}$  mol), TPPTS ( $5.0 \times 10^{-4}$  mol), the phase transfer agent cetyltrimethylammonium bromide, CTAB, ( $8.0 \times 10^{-4}$  mol), water (4 mL) and toluene (10 mL) were placed in the reactor. After a pretreatment for two hours under CO/H<sub>2</sub> (1:1, 20 bar) at 80 °C, the pressure was released and eugenol ( $2 \times 10^{-3}$  mol) was introduced through a ball valve under argon flow. The reactor was pressurized again with CO/H<sub>2</sub> (1:1, 20 bar), let react for 2 h at 100 °C, cooled at room temperature, and then depressurized. The content was transferred into a Schlenk tube under argon flow. The lower (water) phase was collected with a syringe and reintroduced in the reactor. A fresh portion of eugenol ( $2 \times 10^{-3}$  mol) in toluene (10 mL) was introduced and the reactor was pressurized again for a new cycle. The organic phase was analysed by GC.

### 2.4. Product analysis

The products were quantitatively analyzed by gas chromatography (GC) using a Shimadzu GC2010 instrument equipped with a split/splitless injection port and flame ionization detector, fitted with a RestekRtx-wax capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m). Conversion and product distribution were determined by GC. The mass balance was checked employing dodecane as internal standard.

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